Absorption spectrum of a one-dimensional chain with Frenkel's exciton under diagonal disorder represented by hyperbolic defects

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A method is proposed for calculating the absorption spectrum of a long one-dimensional closed-into-a-ring chain with Frenkel's exciton under diagonal disorder. This disorder is represented by the hyperbolic singularities of atomic fission. These defects are shown to lead to a wing in the exciton zone of a chain without defects. The form of the wing does not depend on the relative positions or number of defects and its value is proportional to the sum of the amplitudes of the defects. The proposed method uses only the continual approximation.

1. Introduction

Progress in the theory of translation-symmetric systems is largely due to the possibility of using the Bloch function tools. Switching to the Bloch representation makes it possible to appreciably simplify and, sometimes, even to solve a variety of problems in the physics of translation-symmetric systems. The absence of a similar universal approach in the theory of systems without translation symmetry causes many mathematical difficulties in the analysis of even the simplest systems of this kind. One such system is a model with the Frenkel exciton-type excitations, i.e. a set of two level atoms bound by an interaction capable of carring the excitation from one atom to another. One usually explores only the one-exciton region of energy spectrum, which corresponds to the presence of a single excited atom. If the atoms are arranged symmetrically and have different level splits, the system is called diagonally disordered. Two problems of this kind – the Dyson problem[1] and the Lloyd problem[2] – are two of the very few that allow an exact solution. Approximate methods (such as the coherent potential approximation[3]) were developed for these systems. The quality criterion for these methods is often a comparison with data from computer experi-

ments. However, it is not usually clear why the approximate calculations agrees (if it does) with the numerical calculation. Therefore, in the author's opinion, even abstract models of translation-nonsymmetric systems are of interest if a mathematically convincing solution scheme can be proposed for them. In the present paper, such an abstract model is proposed.

We consider the problem of the Frenkel exciton in an infinitely long chain of two- level atoms that has been closed into a ring. The interatomic interaction and the atomic fission energy as a function of the atom's coordinate are

$$w(z) = V \exp(-|\frac{z}{R}|), \tag{1}$$

and

$$\epsilon(z) = \sum_{r}^{N} \frac{a_r}{(z - R_r)}, a_r > 0 \tag{2}$$

respectively, i.e. diagonal disorder is introdused in the form of a random number N of hyperbolic singularities (hereinafter, hyperbolic defects) which are randomly placed at points R_r and have positive amplitudes a_r (of constatnt sign). In present paper, we propose a method of calculating the absorption spectrum of this chain at zero temperature.

The absorption spectrum of a defectless chain is known to be a singlet. Therfore, changes in the spectrum due to defects are easier to see than changes in the density of states. It is shown herein that hyperbolic defects give rise to a wing in the exciton zone of a defectless chain and that its shape does not depend on the number or relative positions of the defects. Also its size is proportional to the sum of the amplitudes of the defects, $\sum_{r}^{N} a_r$. This result appears to be somewhat unexpected. The calculation was carried out by the method proposed in[4], which uses only the continuation approximation (i.e. the replacement of the lattice sums by integrals). The efficiency of this approach was substantiated in[4]

2. Scheme of the method

In oder to calculate the absorption spestrum of the chain discribed in the Introduction, we use the method proposed in[4]. Here we give the results from that paper. If each spectral line

is thought of as a Lorentz line with width δ, then the absorption spectrum $A(\Omega)$ of a chain with parameters (1),(2) and end coordinates L and $-L$ can be calculated by the formula

$$A(\Omega) = -\frac{1}{\pi}\mathrm{Im}\int\limits_{-L}^{L}\frac{\rho\Psi(z)dz}{E-\epsilon(z)} \tag{3}$$

where $\Psi(z)$ is defined by

$$d^2\Psi/dz^2 + \left(\frac{1}{R}\right)^2\left(\frac{W}{E-\epsilon(z)} - 1\right)\Psi = -\left(\frac{1}{R}\right)^2 \tag{4}$$

Here R is the radius of interaction (1), $W = 2\rho VR$ is the width of the exciton zone of the defectless chain, ρ is the density of the atoms in the chain, ϵ is the atomic fission energy, Ω is the energy of the incident light quantum, and $E = \Omega + i\delta$, $\delta > 0$. For a chain that closed into a ring, the function $\Psi(z)$ must satisfy the cyclicity conditions

$$\Psi(L) = \Psi(-L) \tag{5}$$

$$d\Psi(L)/dz = d\Psi(-L)/dz \tag{6}$$

Integrating (4) over z from L to $-L$ and taking into account (5) and (6), we find that the integral in (3) can be represented as follows:

$$2VR\int\limits_{-L}^{L}\frac{\rho\Psi(z)dz}{E-\epsilon(z)} = \int\limits_{-L}^{L}(\Psi(z)-1)dz \tag{7}$$

Thus the task is redused to calculating the integral $\int\limits_{-L}^{L}\Psi(z)dz$. The idea is to calculate this integral not along the real axis but over semicircle of radius L in the upper half-plane of the complex variable z. This is possible if $\Psi(z)$ does not have singularities (poles or branch points) in the upper half-plane. Next, if $\epsilon(z)$ decreases in the above semicircle, we have the following relationship: the lager the semicircle radius (chain lenth), the more accurately Eq(4) can be solved by perturbation theory on semicircle. As $L \to \infty$, the error tends to zero. It is known[5] that the solution to (4) has no singularities in the upper half-plane of complex z if the function $\frac{W}{(E-\epsilon(z))}$ is a single-valued and has no poles there.

Let us show that this is the case for $\epsilon(z)$ of form (2), where E has a small positive imaginary part. If E is real, the equation $E - \epsilon(z) = 0$ has N real roots $z_k(E)$, $k = 1, ..., N$. If E has small imaginary part term $i\delta$, $\delta > 0$, the roots obtain an increment

$$\delta z_k = \frac{i\delta}{d\epsilon(z_k)/dz}$$

Since $\epsilon(z)$ defined by (2) is decreasing, all roots are shifted to the lower half-plane and, thus, in our case, $\frac{W}{(E-\epsilon(z))}$ does not have poles in the upper half-plane. In the next section, we calculate the spectrum by discribed scheme.

3. Calculation of the spectrum

Let us represent (4) in the form

$$\Psi'' + q^2\Psi + \Delta(z)\Psi = -(1/R)^2 \tag{8}$$

where

$$q^2 \equiv \left(\frac{1}{R}\right)^2 \left(\frac{W}{E} - 1\right) \tag{9}$$

$$\Delta(z) \equiv \left(\frac{1}{R}\right)^2 \frac{W\epsilon(z)}{[E - \epsilon(z)]E} \tag{10}$$

Here q is the wave vector of the exciton with energy E in the defectless chain, the function $\Delta(z)$ describes the defects and decreases in the semicircle of radius L (below we call it large semicircle) in the upper half-plane of complex z. Let us find the solution of (8) in the form $\Psi(z) = \Psi_0(z) + \Psi_1(z) + ...$, where the lower index indicates the order of correction $\Delta(z)$. These corrections obey the following equations:

$$\Psi_0'' + q^2\Psi_0 = -(1/R)^2 \tag{11}$$

$$\Psi_1'' + q^2\Psi_1 = -\Delta\Psi_0 \tag{12}$$

It is not difficult to solve Eqs.(11) and (12). After that, in the approximation under consideration, $\Psi(z)$ becomes

$$\Psi(z) = -\left(\frac{1}{qR}\right)^2 + \left(\frac{1}{qR}\right)^2 \int_L^z \frac{\Delta(\xi)}{q} \sin[q(z-\xi)]d\xi + \tag{13}$$
$$+C_+ \left(e^{iqz} - \int_L^z \frac{\Delta(\xi)}{q} e^{iq\xi} \sin[q(z-\xi)]d\xi \right) +$$
$$+C_- \left(e^{-iqz} - \int_L^z \frac{\Delta(\xi)}{q} e^{-iq\xi} \sin[q(z-\xi)]d\xi \right)$$

All integrations begin at the right end of the chain and go over the large semicircle. Since $\Delta(z)$ is small there, (as $L \to \infty$), we expect that solution (13) in the large semicircle virtually coincides with the exact solution. To find the constants C_+ and C_-, we use the solution (13) and conditions (5) and (6), which is possible because the points $\pm L$ lie in the large semicircle where this solution is valid. The result is the following set of equations for C_+ and C_-:

$$C_+\{I_c(q,q) - 2q\sin(qL)\} + C_-\{I_c(-q,q) - 2q\sin(qL)\} = I_c(0,q)/(Rq)^2 \tag{14}$$

$$C_+\{iI_s(q,q) - 2q\sin(qL)\} + C_-\{iI_s(-q,q) + 2q\sin(qL)\} = iI_s(0,q)/(Rq)^2, \tag{15}$$

where

$$I_c(\alpha,\beta) \equiv \int_L^{-L} \Delta(\xi) e^{i\alpha\xi} \cos[\beta(L+\xi)]d\xi \tag{16}$$

$$I_s(\alpha,\beta) \equiv -\int_L^{-L} \Delta(\xi) e^{i\alpha\xi} \sin[\beta(L+\xi)]d\xi \tag{17}$$

Recall that all integrations are carried out over the large semicircle. We consider q to be real and positive. This means that the **energy E falls within the exciton zone of defectless lattice**. Now we calculate integrals like (16),(17) that appear in (14),(15). Wherever possible, we proceed to the limit $L \to \infty$. Let us explain, for example, how

$$I_s(0,q) = -\int_L^{-L} d\xi \Delta(\xi) \sin[q(L+\xi)]$$

is calculated. In the large semicircle, only the increasing exponent $\exp(-iq(L+\xi))$ should be retained in sine function. On the other hand, this exponent tends to zero in the lower large semicircle. Therefore,

$\int\limits_{L}^{-L} \Delta(\xi) \exp[-iq(L+\xi)]d\xi$

can be calculated over the entire large circle, which is quite easy to do with the help of residues. We give the results of calculating the integrals appearing in (14), (15) below:

$$I_s(0,q) = \pi e^{-iqL} \sum_{\xi} \mathrm{Res}[\Delta(\xi)e^{-iq\xi}] \tag{18}$$

$$I_s(q,q) = \frac{1}{2i} e^{-iqL} \int\limits_{L}^{-L} \Delta(\xi)d\xi \tag{19}$$

$$I_c(0,q) = \pi i e^{-iqL} \sum_{\xi} \mathrm{Res}[\Delta(\xi)e^{-iq\xi}] \tag{20}$$

$$I_c(q,q) = \frac{1}{2} e^{-iqL} \int\limits_{L}^{-L} \Delta(\xi)d\xi \tag{21}$$

Since $I_c(0,q) = iI_s(0,q)$ and $iI_s(q,q) = I_c(q,q)$, then $C_- = 0$ and we do not need the remainig integrals from (14), (15). For C_+, we obtain the following formula:

$$C_+ = \left(\frac{1}{Rq}\right)^2 \frac{2\pi i e^{-iqL} \sum\limits_{\xi} \mathrm{Res}[\Delta(\xi)e^{-iq\xi}]}{e^{-iqL} \int\limits_{L}^{-L} \Delta(\xi)d\xi - 4q\sin(qL)} \tag{22}$$

For the final calculation of $\int\limits_{L}^{-L} (\Psi(z) - 1)dz$, we also need the following integrals that appeared in (13):

$$\int\limits_{L}^{-L} dz \int\limits_{L}^{z} d\xi \Delta(\xi) \sin[q(z-\xi)] = -\frac{i\pi}{q} e^{-iqL} \sum_{\xi} \mathrm{Res}[\Delta(\xi)e^{-iq\xi}] + \frac{1}{q} \int\limits_{L}^{-L} \Delta(z)dz$$

$$\int\limits_{L}^{-L} dz \int\limits_{L}^{z} d\xi \Delta(\xi) e^{iq\xi} \sin[q(z-\xi)] = -\frac{e^{-iqL}}{2q} \int\limits_{L}^{-L} \Delta(z)dz$$

These expressions are derived by expanding the sine into components, integrating by parts, retaining only the exponents that increase in the large semicircle, and proceeding to integration over the hole large circle as when deriving (18)–(21). Taking into account that

$$\int_{L}^{-L} \frac{\epsilon(z)dz}{E-\epsilon(z)} = \frac{i\pi}{E}\sum_r a_r,$$

(integration goes over the large semicircle), it is easy to obtain the following final formula for the absorption spectrum:

$$A(\Omega) = -\frac{1}{\pi}\mathrm{Im}\left(\frac{2L\rho}{E-W} - i\pi\rho\left(\frac{1}{E-W}\right)^2\sum_r a_r\right) \tag{23}$$

$$E = \Omega + i\delta$$

4. Discussion

The first term in (23) yields a singlet and does not depend on the presence of defects. The second term yields a wing in the exciton zone. It is somewhat unexpected that its shape does not depend on the relative positions R_r of the defects. The wing amplitude turns out to be proportional to the sum of the amplitudes of the defects; this calculation has a "physical" level of rigor. For a rigorous calculation , one should write the entire perturbation series in Δ for the solution of (4) and make sure that the influence of all terms of this series, except the above-considered first-order term, tends to zero in the large semicircle as $L \to \infty$. This was done and result (23) turned out to be valid only for real q, i.e., for energies falling within the excitone zone of the defectless chain. For other energy values, the contribution from terms of orders higher than 1 can not be ignored. This behavior should be discussed.

As shown in[4], $\Psi(z)$ is related to the Green's function of the system and, thus, solution (23) could be analytically extended to the range of energies beyond excitone zone of the defectless chain. This would be correct if we were dealing with exact Green's function. However, Eq.(4) is derived in[4] in the continual approximation. Therefore, (23) can yield noticeable deviations from the exact spectrum beyond the excitone zone, where the calculation of the previous section is invalid. Computer analysis confirms this remark.

Figure 1 (there is no figure in this version of the paper, but it is easy to imagine) displays

the logarithmic absorption spectra of two chains with different numbers, positions and amplitudes of the hyperbolic defects at $W = 1, \rho = 1, \delta = 0.02, R = 2$. In all cases the number of particles was 600, i.e., $2L = 600$. The upper part a shows the logarithmic absorption of a chain with five hyperbolic defects. Their positions (numbers of the sites at which atomic fission becomes infinite, i.e., these atoms are effectively absent) are $200, 250, 300, 350, 400$. The respective amplitudes of the defects are $2, 3, 3, 6, 1$. The lower part b shows the same for a chain with two defects having the amplitudes – 5 and 5 and positions – 250 and 350. For each numeric spectrum, a spectrum calculated by (23) (smoothed curves) is given. No fitting (either in amplitude or in shape) was carried out. The energy plotted in units of W. It is evidend from Fig.1 that for $0 < \Omega < 1$ (the excitone zone), the numerical spectra almost completely coincide with the theoretical spectra and the shape of the spectra does not depend on the size or positions of the defects. The discrepancy for $\Omega \approx 1$ is due to the finiteness of the chain because, in this energy range, $q^2(q^2 \approx 0)$ can be comparable to $\Delta(z)$, which is finite in the large semicircle due to the finiteness of the chain. In the region beyond the exciton zone, only agreement "in the mean" is possible (it can be improved by increasing the imaginary part of the energy δ). In this region, the spectrum does depend on the positions and sizes of the defects. It may be possible to apply the proposed approach to more realistic models of chains with defects.

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